

Remarks

This Preliminary Amendment cancels without prejudice original claims 1 to 16 in the underlying PCT Application No. PCT/DE03/01800. This Preliminary Amendment adds new claims 17-36. The new claims, *inter alia*, conform the claims to United States Patent and Trademark Office rules and do not add new matter to the application

In accordance with 37 C.F.R. § 1.125(b), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. § 1.121(b)(3)(ii) and § 1.125(c), a Marked Up Version Of The Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) are respectfully requested.

The underlying PCT Application No. PCT/DE03/01800 includes an International Search Report, dated September 19, 2003, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

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EXHAUST GAS PURIFICATION SYSTEM OF AN INTERNAL COMBUSTION ENGINE AND METHOD FOR PURIFYING THE EXHAUST GASES THEREOF

Field of the Invention

The present invention relates to an exhaust gas purification system of an internal combustion engine having a device for 5 selective catalytic reduction. ~~The invention further, and relates particularly~~ to a method for purifying exhaust gases of an internal combustion engine, in which an exhaust gas stream is passed through a device for selective catalytic reduction.

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Background Information Background Information

To lower the nitrogen oxide content of oxygen-rich exhaust gas, such as that emitted ~~especially~~ by diesel internal 15 combustion engines and by internal combustion engines featuring direct gasoline injection, it is known to introduce a reducing agent into an exhaust tract. A suitable reducing agent is, for example, NH<sub>3</sub>, which may be introduced as a gas into the exhaust gas stream. In ~~that~~such so-called selective 20 catalytic reduction (SCR), the ammonia is selectively reacted with the nitrogen oxides present in the exhaust gas to form molecular nitrogen and water.

The insufficient activity of the known SCR system at exhaust 25 gas temperatures below approximately 250° C is ~~to be~~ regarded as a problem. Upstream installation of an oxidation catalytic converter provides, on the one hand, ~~for~~ a lowering of the content of deactivating hydrocarbons and, on the other hand, ~~for~~ oxidation of NO to NO<sub>2</sub>, which leads overall to a marked 30 increase in NO<sub>x</sub> conversion at exhaust gas temperatures above

approximately 200° C. Especially when used in passenger automobiles, however, phases having such low exhaust gas temperatures occur relatively frequently, as is illustrated by a mean catalytic converter temperature of less than 180° C in 5 the known MVEG test cycle (MVEG: Motor Vehicles Emissions Expert Group; an expert group of the European Commission).

To ensure good distribution of the reducing agent over the SCR catalyst, a mixing section of approximately 40 cm, may be 10 provided, where appropriate, with a mixing device, may be providedwhere appropriate. A mixing device of that kind for an exhaust gas purification system is described in the earlier published German Patent Application having the file reference 101 31 803.0. In that document, which discloses that 15 a mixing body disposed in the exhaust pipe has a gas impingement surface and a jet impingement surface, so that exhaust gas flowing out of the internal combustion engine may impinge upon the gas impingement surface, and reducing agent, which may be fed transversely to the exhaust gas stream, may 20 impinge upon the jet impingement surface.

#### Summary of the Invention Summary

An exhaust gas purification system configured in accordance 25 with the present invention includes at least one oxidation catalytic converter disposed in an exhaust gas duct of an internal combustion engine, and at least one device for selective catalytic reduction of the exhaust gases, which device is installed downstream of the oxidation catalytic 30 converter. The exhaust gas purification system further includes a feed device for feeding reducing agent into the exhaust gas stream and admixing it therewith upstream of the device, or in the device, for selective catalytic reduction (SCR catalytic converter). According to the invention, the

exhaust gas purification system has a switch-over device and/or a further feed device for selectively feeding reducing agent into the exhaust gas stream upstream of, or inside, the at least one oxidation catalytic converter. Using such a

5 configuration of the oxidation catalytic converter and the so-called SCR catalytic converter, it is possible to obtain a reduction in the NO<sub>x</sub> emission ~~limit values to a level~~ below a ~~quantity of emitted NO<sub>x</sub> that which~~ ensures compliance with the permissible exhaust gas standards during the MVEG test cycle.

10 Such a reduction in NO<sub>x</sub> emissions may be achieved by additionally utilizing the temperature-resistant oxidation catalytic converter, which is already present and ~~which is~~ used for nitrogen oxide oxidation, for the purpose of NO<sub>x</sub> reduction during a cold start phase. When installed close to

15 the engine, the oxidation catalytic converter will ~~already~~ ~~have reached~~ reach a temperature of more than 100° C after about 50 seconds, which is sufficient for NO<sub>x</sub> reduction using NH<sub>3</sub> or a reducing agent that splits off NH<sub>3</sub>.

20 Oxidation catalytic converters mainly have noble metals, such as platinum, as the active component. Oxidation reactions of hydrocarbons, carbon monoxide and nitrogen monoxide are thereby promoted even at low temperatures. If NH<sub>3</sub> is injected as the reducing agent, these catalytic converters exhibit a

25 relatively strong ~~de~~ NO<sub>x</sub> reduction activity even at temperatures below 100° C.

If a configuration having a switch-over device instead of a separate feed device for the oxidation catalytic converter is

30 chosen, this ~~can~~ may reduce assembly costs. The present invention provides ~~likewise~~ includes, however, an example embodiment having separate and separately controllable feed devices for reducing agent.

The switch-over device for selectively feeding the reducing agent into the exhaust gas stream upstream of, or in, the oxidation catalytic converter, or into the SCR catalytic converter, may be in the form of a valve, especially a 3/2-way valve. In that manner, the reducing agent may be fed selectively to the oxidation catalytic converter or to the SCR catalytic converter, according to the temperature level that these converters have reached in driving operation.

10 One embodiment of the invention provides for the switch-over device to be in the form of a mixing valve. In that manner, it is possible for reducing agent to be admitted to the oxidation catalytic converter and the SCR catalytic converter simultaneously during a transition period. Using such a mixing

15 valve, it is possible to avoid an abrupt switch-over, so that, depending upon the operating temperatures reached by the catalytic converters, an optimum purifying effect may be obtained.

20 The switch-over device is preferably may be temperature-controlled, so that, during a cold start phase with exhaust gas temperatures that are still low, reducing agent may be admitted to the oxidation catalytic converter and, after a warm-up phase, to the SCR catalytic converter.

25 The feed device preferably includes may include in each case a metering device for quantity metering and nozzles for distributing and atomizing the reducing agent in the exhaust gas stream.

30 Preferably, the at least one oxidation catalytic converter is disposed in the immediate vicinity of an exhaust gas outlet of the internal combustion engine, with the result that it

reaches relatively high temperatures and thus achieves a high purifying effect after only a short time.

~~As the~~ The reducing agent may be, ~~there comes into~~  
5 ~~consideration~~, for example, an ammonia-containing or ammonia-releasing substance capable of effecting NO<sub>x</sub> reduction. Examples of such a substance ~~that come into~~ ~~consideration~~ are urea and ammonium carbamate.

10 In a method according to the present invention for purifying exhaust gases of an internal combustion engine, ~~in which~~ ~~method~~ an exhaust gas stream is passed through at least one oxidation catalytic converter disposed in the exhaust gas duct and through at least one device for selective catalytic

15 reduction (SCR catalytic converter) installed downstream of the oxidation catalytic converter, ~~and there is fed to the exhaust gas stream a reducing agent which, according to the present invention, is selectively fed to the exhaust gas stream upstream of, or inside, the at least one oxidation~~

20 catalytic converter. The reducing agent ~~is~~may be selectively fed to both catalytic converters simultaneously or to only one of the catalytic converters. The reducing agent ~~is~~may be distributed and atomized ~~preferably~~ by a nozzle.

25 One embodiment of the method according to the present invention provides for temperature-controlled feeding of the reducing agent into the oxidation catalytic converter and/or into the device for selective catalytic reduction.

30 If NH<sub>3</sub> is admitted to the oxidation catalytic converter, the latter exhibits a relatively pronounced ~~de~~ NO<sub>x</sub> NO<sub>x</sub> reduction activity at temperatures below 100° C. The useful temperature window for NO<sub>x</sub> reduction is relatively narrow, however, since above approximately from 250° C to 300° C nitrogen reduction no

longer takes place but, rather, additional nitrogen oxide production takes place as a result of oxidation of NH<sub>3</sub>. In addition, relatively high N<sub>2</sub>O selectivities may possibly be observed. It must, therefore, be ensured that reducing agent 5 is admitted to the oxidation catalytic converter only in a starting phase (in the MVEG test, only up to about 350 s). Preferably For example, the reducing agent is fed into the oxidation catalytic converter at exhaust gas temperatures of less than approximately from 150° C to 200° C in the oxidation 10 catalytic converter.

After such a period of time, the SCR catalytic converter will normally also have reached its operating temperature and injection of reducing agent is switched to the SCR catalytic 15 converter. That may be done at temperatures of approximately from 150° C to 200° C in the SCR catalytic converter. Metering of reducing agent onto the oxidation catalyst is possible in principle at operating points with a low exhaust gas temperature - that is to say, not only in the case of cold 20 starting - and promises provides a very effective NO<sub>x</sub>-lowering potential in cases where only insufficient activity is achieved with the SCR catalytic converter. With injection upstream of the oxidation catalytic converter up to a time of about 600 s, therefore, a marked increase in conversion by the 25 exhaust gas purification system ~~is to~~ may be achieved. A suitable, sensible switch-over point of the temperature-controlled switch-over valve may lie at ~~from~~ 100 to 200° C, preferably e.g., at ~~from~~ 130 to 180° C.

30 A practical An example embodiment of the system according to the present invention may, for example, provide a 3/2-way switch-over valve which is operated in dependence upon the catalytic converter temperatures and the operating point of the engine. Equipping an existing system in that manner is

relatively simple and ~~can~~may be done with only little expenditure. The catalyst system, the temperature sensors and the metering system are already present, and ~~nor is it~~ necessary for those components to be modified. Only only the 5 switch-over valve and the reducing agent feed line upstream of the oxidation catalytic converter ~~have~~need to be ~~retrofitted~~implemented. By a suitable metering strategy, it is possible for effective reduction of the nitrogen oxides to be achieved over an entire test cycle (MVEG cycle). In the MVEG 10 test, it is possible for an increase in NO<sub>x</sub> conversion of approximately 40% to be achieved, with the result that in the case of lowered untreated emissions it is even possible to meet the relatively strict U.S. standards.

15 The oxidation catalytic converter may, in a ~~preferred~~an example embodiment, be in the form of a catalytically coated particle filter. The catalytic coating of the particle filter acts in this case similarly to the coating of a ~~known~~an oxidation catalytic converter. It is furthermore possible for 20 a separate particle filter, which effects filtering of the soot particles, to be provided between the oxidation catalytic converter and the SCR catalytic converter.

25 The present invention is described in detail below in preferred exemplary embodiments with reference to the associated drawings, in which: Brief Description of the Drawings

30 Figure 1 is a ~~diagrammatic~~schematic illustration of an internal combustion engine having an exhaust gas after-treatment unit in an exhaust gas duct.

35 Figure 2 is a ~~diagrammatic~~schematic illustration of the internal combustion engine according to Figure 1 in a first operating position.

Figure 3 shows the internal combustion engine according to Figure 1 in a second operating position.

5 Figure 4 ~~shows~~ is a chart showing typical temperature variations of the components of the exhaust gas purification system during a test cycle.

10 Figure 5 ~~shows~~ is a chart showing typical NO<sub>x</sub> emission values during a test cycle, and.

Figure 6 is a ~~qualitative diagram~~ chart illustrating the SCR activity of an oxidation catalytic converter.

15 Detailed Description

Figure 1 shows an exhaust gas purification system according to the present invention ~~in diagrammatic form~~. In that ~~diagram, Figure 1~~, an oxidation catalytic converter 4 and a 20 device for selective catalytic reduction, referred to as SCR catalytic converter 6, are disposed in an exhaust gas duct 28 of an internal combustion engine 2. Internal combustion engine 2 has an intake duct 21 for supplying fresh mixture 22, and outlet ducts 26 which are combined in a manifold 27 to form 25 exhaust gas duct 28. Disposed in the exhaust gas duct is an exhaust gas turbine 24 of an exhaust gas turbocharger 23, which turbine 24 is coupled via a shaft 25 to a compressor, not shown here. Exhaust gas turbocharger 23 is optional and serves to improve the performance and exhaust gas emission 30 characteristics of internal combustion engine 2.

Internal combustion engine 2 ~~is preferably~~ may be a diesel internal combustion engine featuring auto-ignition or a gasoline engine featuring direct fuel injection. Both types of

engine emit a relatively oxygen-rich exhaust gas. Exhaust gas stream 29 passes successively through oxidation catalytic converter 4 and SCR catalytic converter 6 and leaves the exhaust gas purification system as purified exhaust gas 14

5 which is passed into the open air via a muffler (not shown). The exhaust gas purification system further includes a feed device 8 for feeding a reducing agent 81 into exhaust gas stream 29. Feed device 8 includes a switch-over device 83 and also a first connection line 84, which is connected to a first 10 nozzle 85, and a second connection line 86, which is connected to a second nozzle 87. First nozzle 85 is disposed upstream of oxidation catalytic converter 4 in exhaust gas duct 28 and serves to finely distribute and atomize reducing agent 81 upstream of oxidation catalytic converter 4. Second nozzle 87 15 is disposed upstream of SCR catalytic converter 6 and downstream of oxidation catalytic converter 4 and serves to feed reducing agent 81 into exhaust gas stream 29 upstream of SCR catalytic converter 6.

20 First and second connection lines 84, 86 open into switch-over device 83 which is able to provide for selective distribution of the reducing agent to first and/or second connection line 84, 86. Switch-over device 83 ~~is~~may be controlled preferably temperature-dependently, so that, in a cold running phase, 25 reducing agent 81 may be admitted to oxidation catalytic converter 4 and, after a certain temperature has been reached, to SCR catalytic converter 6.

Figure 2 illustrates the cold running phase of the exhaust gas 30 purification system, in which reducing agent is admitted only to first nozzle 85. This is illustrated by arrow 81 along first connection line 84.

Figure 3 illustrates the subsequent phase, in which the catalytic converters have already reached a predetermined operating temperature. In this case, reducing agent 81 is admitted to second connection line 86 and second nozzle 87.

5 This is illustrated by arrow 81 along second connection line 86.

A typical transition temperature may lie at approximately from 100° C to 200° C, preferablye.g., at about from 130 to 180° C,

10 above which a switch-over to admission of reducing agent 81 to SCR catalytic converter 6 may take place. A switch-over may also be made in an advantageous manner by a mixing valve, which is able to provide for simultaneous admission to oxidation catalytic converter 4 and SCR catalytic converter 6

15 in the transition temperature range.

~~Also included within An alternative configuration according to the present invention is an alternative configuration that provides two separate feed devices for the oxidation catalytic converter and the SCR catalytic converter.~~

In an alternative embodiment, oxidation catalytic converter 4 may be a catalytically coated particle filter which, by virtue of its catalytic coating, has the same effect as a known an oxidation catalytic converter. In addition to the configuration shown, a separate particle filter may be disposed between oxidation catalytic converter 4 and SCR catalytic converter 6. That particle filter produces a further improvement in the purifying effect on the exhaust gases.

30

Figure 4 illustrates typical temperature variations of the oxidation catalytic converter and the SCR catalytic converter during a standardized test cycle. The so-called MVEG test will be referred to hereinafter as an example of a test cycle. The

time in seconds is plotted on the horizontal axis and the temperature in ° C on the vertical axis. It will be apparent that the oxidation catalytic converter (upper, jagged curve) is capable of reaching temperatures of up to 200° C after a 5 period of as little as approximately 150 seconds. The temperature of the SCR catalytic converter (lower, undulating curve) is still distinctly below 150° C after 300 seconds. At those temperature ranges in the SCR catalytic converter, feeding of reducing agent will not yet produce satisfactory 10 reduction results for NO<sub>x</sub>. Since the oxidation catalytic converter reaches temperatures of more than 100° C after only a few seconds, it is possible for good NO<sub>x</sub> reduction to be already achieved by feeding reducing agent upstream of, or into, the oxidation catalytic converter. The dashed vertical 15 line at approximately 300 seconds represents the earliest sensible time to commence NH<sub>3</sub> injection upstream of the SCR catalytic converter. The continuous vertical line at approximately 350 seconds represents the start of effective 20 NO<sub>x</sub> reduction by the SCR catalytic converter in the MVEG test cycle.

Figure 5 illustrates the cumulative emission of NO<sub>x</sub> over time in various systems for exhaust gas purification. The time in seconds is shown on the horizontal axis and the cumulative 25 amount of emitted NO<sub>x</sub> is shown on the vertical axis. It will be apparent that, by injecting reducing agent upstream of the oxidation catalytic converter and in the SCR catalytic converter in accordance with the present invention, it is possible for emissions of NO<sub>x</sub> to be markedly reduced.

30 Lowermost curve 20 illustrates that only with the system according to the present invention is it possible to comply with the MVEG limit value of 0.9 g of NO<sub>x</sub>. Discontinuous curve 22 extending above the latter characterizes the curve for NO<sub>x</sub>

emissions in a conventional system composed of oxidation catalytic converter and SCR catalytic converter arranged in series (so-called conventional VR system without switch-over).  
5 Curve 24 illustrates the emissions of a system that provides feeding of reducing agent merely upstream of the oxidation catalytic converter. At first, good reduction takes place, whereasbut the elevated temperatures at and beyond approximately 800 seconds prevent effective  $\text{NO}_x$  reduction. From that point in time, the  $\text{NO}_x$  emissions rise steeply and  
10 even approach the values of untreated emissions (curve 26), since, at and above approximately from 300 to 350° C, an additional quantity of  $\text{NO}_x$  is produced.

Figure 6 illustrates the  $\text{NO}_x$ -reducing effect of the oxidation catalytic converter overas a function of temperature. It will be apparent that, at and above a temperature of approximately 200° C,  $\text{NO}_x$  reduction falls markedly and that, at and above temperatures of approximately 350° C,  $\text{NO}_x$  is even additionally produced. The temperature is shown on the horizontal axis and  
20 the conversion is shown on the vertical axis. It will be apparent that the conversion of  $\text{NO}_x$  declines markedly at and above a certain temperature (approximately 200° C). That is the reason why, after the cold running phase, the feeding of reducing agent upstream of the oxidation catalytic converter  
25 mustshould be discontinued and reducing agent may continue to be fed only upstream of the SCR catalytic converter.

Abstract

ABSTRACT

An exhaust gas purification system for purifying the exhaust gas of an internal combustion engine, especially an internal combustion engine featuring auto-ignition and/or direct fuel injection, is described, provided. which The system includes at least one oxidation catalytic converter disposed in an exhaust gas duct of the internal combustion engine, at least one device for selective catalytic reduction of the exhaust gases which is installed downstream of the oxidation catalytic converter, and a feed device for feeding reducing agent into the exhaust gas stream upstream of, or in, the device for selective catalytic reduction. A switch-over device (83) is provided for selectively feeding reducing agent (81) into the exhaust gas stream (29) upstream of, or inside, the at least one oxidation catalytic converter (4). A corresponding method for purifying the exhaust gas of an internal combustion engine (2) is also provided.

20 (Figure 1)